United States Patent Office

3,218,168

Patented Nov. 16, 1965

3,218,168

HEAT AND PHOTOSENSITIVE COPY SHEET

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No Drawing. Filed Oct. 15, 1962, Ser. No. 230,735
9 Claims. (Cl. 96—85)

This invention relates to the copying of graphic originals and has particular reference to visibly heat-sensitive copy-sheets useful for such purposes. More particularly, the invention is concerned with visibly heat-sensitive copy-sheets capable of being desensitized by exposure to actinic radiation.

One well-known and commercially important method of making copies of typewritten correspondence and like graphic originals is known as the thermographic copying process. As commonly employed, it involves brief irradiation of the differentially radiation-absorptive original, while in heat-conductive association with the copy-sheet, with high-intensity radiation. Image areas of the copy-sheet corresponding to the thus preferentially heated radiation-absorptive inked image areas of the original are visibly changed. Background areas remain unchanged and still visibly heat-sensitive.

Heat-sensitive copy-sheets useful in thermographic copying processes and capable of undergoing permanent visible change when briefly heated to a conversion temperature within the commercially desirable range of about 60–150° C. are well known in the graphic arts. In some of these products the visible change results from chemical reaction of inter-reactive components maintained in intimate association with each other by a film-forming binder. In others the visible change occurs upon the clarification of an opalescent layer of particulate or discontinuous components, held in place by minor amounts of film-forming binder, into a continuous transparent covering through which a colored background may be seen.

The art has recognized that the film-forming binders employed in both the chemical and the physical type thermographic copy-sheets are useful for retaining the reactive or fusible components in proper relationship and on the supporting backing. These binder materials are also helpful in preventing transfer of active materials to surfaces with which the copy-sheet comes in contact during the thermographic copying process. For such purposes it has generally been found desirable to employ polymers which do not fuse at the conversion temperature employed in thermocopying, such conversion temperature being normally within the previously indicated commerically desirable range of about 60–150° C.

While copies prepared on these heat-sensitive copy-sheets are stable and hence permanent under normal handling and storage, the still unchanged background areas obviously remain sensitive to further heating at the original conversion temperature within the stated approximate 60–150° C. range.

The present invention provides heat-sensitive copy-sheets of both the physical and chemical types which like the earlier types require only the brief application of a heat-image, e.g., by thermographic copying processes, to produce a visible copy, but which in addition may be stabilized against further heat-induced change at their original conversion temperature by simple irradiation with actinic light. Alternatively, copy-sheets of the present invention may first be exposed to a desensitizing light pattern, for example through a stencil or a photographic transparency, and then subjected to uniform overall heating to cause a visible change only in the unexposed areas. In either case, liquids, solutions, vapors, additional sheet

materials, or other aids are not essential in producing accurate, legible, and fully stable copies of a wide variety of graphic originals.

Under thermographic copying practice with copy-sheets of the prior art, fusion of the binder component of the chemically inter-reactive or particulate fusible heat-sensitive layers does not appear to occur, and binder components for thermographic heat-sensitive copy-sheet products are indeed normally selected as being non-fusing at temperatures attained in the copying process. Whether the visible change occurs as a result of localized softening of the binder itself or of a blend of binder and other constitutents, or as a result of local shrinkage or solubilizing or chemical change or other heat-induced alteration of the binder component, or solely through fusion or fluidification of non-binder components, or by some other mechanism, is not known with certainty. Unexpectedly, and regardless of theoretical mechanisms, the use of soluble, solid organic thermoplastic photosensitive film-forming materials in heat-sensitive copy-sheet structures as herein described has now resulted in copy-sheet products which are fully heat-sensitive as required in the thermographic copying process while being capable of desensitization against further heat-induced change.

The practice of the invention will now be described for convenience in terms of specific illustrative but non-limiting examples in which proportions are designated as parts or percentages by weight.

Example 1

Visibly opaque heat-transparentizable coatings utilizing a photocrosslinkable polymer material provide useful stabilizable heat-sensitive copy-sheet products.

A solution consisting of:

	Parts
Polyvinyl cinnamate	10
Chloroform	298
Normal butanol	41

is applied at a thickness of five mils onto 50 lb. basis weight black radiation-absorptive cellulosic paper containing approximately one quarter its weight of carbon black and about 4% of a butadiene-styrene copolymer serving as a polymeric binder for the radiation-absorptive pigment. The coating is allowed to dry slowly under normal room conditions and subdued light, resulting in an opalescent blush layer which effectively conceals or masks much of the color of the underlying black paper carrier sheet.

The polyvinyl cinnamate is a yellowish thermoplastic film-forming photosensitive polymer material soluble in methyl ethyl ketone. It is commercially obtainable from Eastman Kodak Company at the filing date of this application as a 10% solution under the trademark "Photo Resist." As thus obtained, the polyvinyl cinnamate polymer has a saponification value of about 168. The dry polymer, obtained in the form of small crumb-like particles by precipitation with water from the 10% solution followed by drying, has a softening range of about 110–120° C., which may be raised to about 135°–145° C. by a two-minute exposure of the water-precipitated dried crumb-like polymer to radiation from a BH–6 high pressure mercury arc lamp held six inches away. This radiation is predominantly within the ultraviolet portion of the spectrum.

In this and similar cases the softening point is conveniently determined on a Fisher-Johns melting point apparatus, the samples being placed between two thin microscope cover glasses and observed through a binocular microscope. A five-gram weight is placed upon the upper cover glass. The softening point is taken as that temperature at which the solid particle just begins to flow out. The rate of temperature rise is about one degree per minute, and in no case greater than three degrees per minute.

The preparation of suitable polyvinyl cinnamate is described in British Patent 713,947. Essentially it comprises the esterification at moderately elevated temperature of highly saponified polyvinyl acetate in pyridine with cinnamoyl chloride added in small portions. The reaction product is extracted with methyl ethyl ketone, precipitated and washed with water, dried, and again dissolved to the desired consistency.

The opalescent blush layer transparentizes when the heat-sensitive copy-sheet is held in momentary contact with a metal test bar heated to 120° C., permitting the colored backing to be seen through the transparentized coating. The colored areas remain clearly visible on cooling.

A graphic original, typewritten on one side of translucent onion-skin paper, is placed smoothly upon the coated surface of the copy-sheet. Ultraviolet light is applied for two minutes through the onion-skin original from a BH–6 lamp held six inches away. Contacting the thus irradiated copy-sheet for a few seconds with a metal roller or platen heated to 130° C. selectively transparentizes the non-irradiated image portions of the opalescent coating to form a positive copy having black images on a light gray background. The ultraviolet irradiated background areas do not transparentize when briefly subjected to test bar temperatures up to at least about 155° C.

Example 2

Desensitizable heat-sensitive transparentizable coatings may alternatively be applied to transparent backings to provide heat-sensitive copy-sheets which are particularly useful in preparing projection transparencies from differentially radiation-absorptive graphic originals.

A photocrosslinkable polymer material is first prepared as follows:

Twenty ml. of an aqueous solution containing 0.01 moles of the tetramethyl ammonium salt of polypropanesultam (formed from stoichiometric amounts of tetramethyl ammonium hydroxide and polypropane sultam) is heated to 80° C. while stirring, and to the hot solution is added 0.01 mole of cinnamyl chloride. The reaction mixture is maintained under mild agitation at 80° C. for 20 minutes, whereupon the solution is made slightly acid by the controlled addition of concentrated hydrochloric acid. A rubbery mass of polymer thereupon separates from the solution. The rubbery product is washed with water, ethanol and water, separately and in that order. The photocrosslinkable thermoplastic film-forming polymer material thus obtained is dried in vacuo for two hours at room temperature and then for two hours at 40° C., under dark conditions. During the process the color changes from white to light tan. The N-cinnamyl polypropanesultam thus obtained has a softening range of about 110–115° C., and is about 70 percent alkylated. The softening range is raised to about 140–150° C. after a two-minute exposure to the ultraviolet radiation from a BH–6 lamp held six inches away.

One part of the N-cinnamyl polypropane sultam is dissolved in ten parts dimethyl formamide. The solution is applied at a thickness of four mils on a 2-mil "Mylar" tensilized polyester film backing and allowed to dry under room conditions and subdued light for approximately five minutes. While the coated side is still tacky to the touch, it is exposed briefly to a jet of steam whereupon the coating develops a semi-opaque non-tacky blush. Further drying results in a semi-opaque dried blush layer which is permanently transparentized when the coated sheet material is held in momentary contact with a metal test bar heated to 110° C.

The coated side of the sheet material is placed against the typewritten side of an opaque original and is front-printed by brief exposure to intense radiation applied through the copy-sheet in a thermographic copying machine; a negative transparency is obtained, having clarified image areas and white opaque background areas which are still transparentizable when briefly heated to 110° C.

Ultraviolet light from a BH–6 lamp held six inches away is applied for two minutes onto the coated side of the imaged transparency. The background areas thereafter remain opaque and will not transparentize when subjected to test bar temperatures as high as 155° C. The copy is effective as a projection transparency for use in overhead projectors.

Example 3

The two previous examples have utilized as the soluble, solid thermoplastic photosensitive film-forming material an unsaturated polymer that is in and of itself inherently photocrosslinkable and undergoes an increase in softening temperature under the influence of actinic radiation. However, when a photoactivatible auxiliary component is employed in conjunction therewith, normally light-stable saturated polymers may similarly be made increasingly resistant to heat-softening under the influence of actinic radiation and thus the mixture may serve as a photosensitive material useful for the purposes of this invention. One photoactivatible auxiliary component, which is useful in the further polymerization of many normally light-stable saturated polymeric materials, is 2-methyl anthraquinone.

A solution is prepared consisting of:

	Parts
2-methyl anthraquinone	6
Ethyl cellulose ("N–200")	100
Denatured ethanol	1900
Water	600

The "N–200" ethyl cellulose is a white granular thermoplastic normally light-stable film-forming saturated polymer soluble in ketones and other solvents. It has a 47½–49% ethoxy content, a softening range of 155–170° C., and a viscosity of 200 cps. at 25° C. measured as a 5% solution in an 80:20 mixture of toluene and ethanol.

A portion of the above solution is spread in a thin layer on an inert smooth substrate and allowed to dry under room conditions and subdued light, resulting in a white readily pulverizable homogeneous residue. The residue is removed from the substrate and pulverized by grinding with a mortar and pestle. It has a softening point of 160° C. Ultraviolet light from a BH–6 lamp held six inches away is applied for two minutes onto the pulverized residue material. The irradiated material has a softening point within the range of 185–190° C. showing that the combination of ethyl cellulose and 2-methyl anthraquinone is effectively a photocrosslinkable film-forming material.

Another portion of the solution is applied at a thickness of three mils on a 2-mil "Mylar" tensilized polyester film backing and allowed to dry slowly under room conditions and subdued light, resulting in an opalescent blush layer. When the coated sheet material is held in momentary contact with a metal test bar heated to 155° C., the opalescent blush layer transparentizes.

The coated side of the sheet material is placed against the typewritten side of an opaque original and is front-printed by brief exposure of the differentially radiation-absorptive printed original to intense radiation applied through the copy-sheet in a thermographic copying machine; a negative transparency is obtained, having clarified image areas and white opaque background areas which are still transparentizable when briefly heated to 155° C.

Ultraviolet light from a BH–6 lamp held six inches away is applied for two minutes onto the coated side of the imaged transparency. The background areas thereafter remain opaque and will not transparentize when subjected to test bar temperatures as high as 170° C. The copy is effective as a projection transparency for use in overhead projectors.

In a modification of the foregoing copy-sheet, a solution consisting of:

	Parts
2-methyl anthraquinone	6
Ethyl cellulose ("N-200")	100
Acrylamide	40
N,N'-methylene bis acrylamide	40
Denatured ethanol	1900
Water	600

is applied at a thickness of three mils on a similar 2-mil "Mylar" film backing and allowed to dry slowly under room conditions and subdued light, resulting in an opalescent blush layer. When the coated sheet material is held in momentary contact with a metal test bar heated to 155° C., the opalescent blush layer transparentizes.

The coated side of the thermographic sheet material is placed against the typewritten side of an opaque original and is front-printed by brief exposure to intense radiation in a thermographic copying machine; a negative transparency is obtained, having clarified image areas and white opaque background areas which are still transparentizable when briefly heated to 155° C.

Ultraviolet light from a BH-6 lamp held six inches away is applied for two minutes onto the coated side of the imaged transparency. The background areas thereafter remain opaque and will not transparentize when subjected to test bar temperatures as high as 190° C., a 20° C. increase in irradiated background transparentization temperature over the sheet material previously described in this example. The increased stability of the background toward heat is believed due to the particular efficiency of the photoactivatible auxiliary component herein employed, i.e., the acrylamides in admixture with 2-methyl anthraquinone. The copy is similarly effective as a projection transparency for use in overhead projectors.

A further modification employs a solution consisting of:

	Parts
2-methyl anthraquinone	6
Ethyl cellulose ("N-200")	100
Tetraethylene glycol dimethacrylate	20
Denatured ethanol	1900
Water	600

The solution is applied at a thickness of three mils on a 2-mil "Mylar" polyester film backing and allowed to dry slowly under room conditions and subdued light, resulting in an opalescent blush layer. The coating transparentizes when the sheet is placed in contact with a metal test bar at 115° C., i.e. to a temperature some 40° C. lower than is required to transparentize the coating prepared of ethyl cellulose in the absence of the tetraethylene glycol dimethacrylate.

The coated side of the film is placed against the typewritten side of an opaque original and is subjected to front-printing as previously described; a negative transparency is obtained, having clarified image areas and white opaque background areas which are still transparentizable when briefly heated to 115° C.

Ultraviolet light from a BH-6 lamp held six inches away is applied for two minutes onto the coated side of the imaged transparency. The background areas thereafter remain opaque and will not transparentize when subjected to test bar temperatures as high as 190° C., again a 20° C. increase in the transparentization temperature of the irradiated background areas over the initially produced sheet material of this example. Thus, the photoactivatible auxiliary component herein employed i.e. the mixture of 2-methyl anthraquinone and tetraethylene glycol dimethacrylate, has the unusual ability both to lower the transparentization temperature of the pre-irradiated sheet material and to increase the transparentization temperature of the irradiated background areas. The copy is effective as a projection transparency for use in overhead projectors.

Alternatively, the copy-sheets of the present example may first be exposed to a desensitizing light pattern through a positive transparency, and then subjected to uniform overall heating to cause a visible change in the unexposed and still heat-sensitive background areas. For example, the coated side of the sheet material initially produced in this example is placed against the typewritten side of a translucent onion-skin original, and ultraviolet light is applied for two minutes through the onion-skin orignial from a BH-6 lamp held six inches away. Contacting the thus irradiated sheet material for a few seconds with a platen heated to 165° C. selectively transparentizes the non-irradiated image portions of the opalescent coating; the light-exposed background areas remain white and opaque.

Example 4

A solution of 100 parts of polyethyl methacrylate having a softening point of 180° C., 20 parts of tetramethylene glycol dimethacrylate, and 6 parts of 2-methyl anthraquinone in acetone sufficient to provide a concentration of 8% non-volatiles is coated on 2-mil "Mylar" polyester film at a coating orifice of 3 mils and dried under subdued light. Just prior to complete evaporation and while still tacky to the touch, the coating is exposed briefly to a jet of steam to develop a semi-opaque blush surface. The dried coating transparentizes when heated by brief contact with a metal test bar at 120° C. The coating is exposed through a photographic negative to the radiations from a BH-6 lamp at 6 inches for 2 minutes and is then briefly heated at 130–140° C. to transparentize the unexposed areas, forming an effective projection transparency. The exposed areas are capable of withstanding temperatures up to about 160° C. without transparentizing.

Example 5

A copy-sheet is prepared and tested as described in Example 4 except that the polyethyl methacrylate is replaced with an equal weight of copolymer of vinylidene chloride and acrylonitrile having a softening point of 200° C. The opaque coating transparentizes at 150° C. After irradiation the coating withstands temperatures up to about 200° C. After irradiation through the photographic negative transparency, development of the projection transparency is conveniently achieved by heating the sheet at 160° C.

Example 6

An eight percent solution in acetone of 100 parts of N-200 ethyl cellulose, 10 parts of thiourea. and 1.5 parts of rose bengal is coated at 3 mils on Mylar polyester film, dried, and opacified with steam as described in Example 4. The coating transparentizes on heating to 155° C. The sheet is exposed through a photographic negative to radiation from a 500 watt tungsten filament projection lamp for eight minutes at an intensity of 10,000 foot candles and is then heated at 160° C. whereupon a copy of the negative is obtained having transparent areas corresponding to the opaque areas of the negative. The opaque areas of the copy withstand temperatures up to about 165–170° C. before transparentizing.

The radiation from the projection lamp employed in this example is largely in the visible region.

Example 7

Mixtures of conventional binder materials with thermoplastic photocrosslinkable polymer materials provide effective transparentizable opaque heat-sensitive coatings and stabilizable heat-sensitive copy-sheets.

A solution consisting of:

	Parts
Polyvinyl cinnamate	10
Polymethyl methacrylate "Acryloid K-120"	10
Butyl stearate	1
Methyl ethyl ketone	380

is applied at a thickness of four mils onto 25-lb. transparent glassine paper and dried at room temperature. The resultant coating is substantially opaque. The coated sheet is adaptable for front-printing in a thermographic copying machine to provide a copy of a graphic original in the form of a positive transparency having light-scattering white-appearing background areas. The nearly opaque background clarifies when held in momentary contact with a 125° C. test bar. Exposure to ultraviolet radiation as described in Example 1 increases the temperature requirement for transparentization to at least about 150° C.

An improved copy-sheet construction is made by applying a thin color coating over the heat-transparentizable coating, and drying at room temperature. The second coating serves to protect the heat-sensitive layer and to provide a visible color at image-forming transparentized areas when the copy is viewed through the transparent glassine paper. Irradiation of the heat-transparentizable coating with ultraviolet through the glassine paper backing renders the normally heat-transparentizable background areas stable against further heating up to temperatures of at least 150° C.

The color coating is prepared by mixing together

	Parts
"Diane blue" infra-red-transmitting blue lake pigment	2
Ethyl cellulose	2
Commercial grade heptane	11
Toluene	77
Glacial acetic acid	0.003

The coated side of the sheet material is placed against the typewritten side of an opaque original and the composite is subjected to front-printing in a thermographic copying machine; a positive copy is obtained, having blue-appearing image areas and white opaque background areas which are still capable of assuming a colored appearance when briefly heated to 110° C.

Ultraviolet light from a BH–6 lamp held six inches away is applied for two minutes through the transparent film backing of the imaged copy-sheet. The background areas thereafter remain white in appearance and do not convert to the blue appearance when subjected to test bar temperatures as high as 155° C.

An extremely thin and highly heat-sensitive modification of the copy-sheet of Example 7 is obtained by applying the coatings to a temporary carrier, such as a polished metal drum, from which the thin dried self-sustaining heat-sensitive film product is subsequently removed by stripping.

Other pigments, dyes or other coloring agents may be used in place of the specific pigment named. Infra-red-transmitting colorants are required where front-printing with infra-red radiation is employed.

Example 8

Photocrosslinkable materials are effective in providing for the desensitization of normally heat-sensitive copy-sheet products which operate through the heat-induced localized physical offsetting of colored materials.

The following mixture consisting of:

	Parts
Polyvinyl cinnamate	4
Castor wax	4
Triphenyl phosphate	4
"Diane Blue" pigment	1
Methyl ethyl ketone	20
Methanol	10

is ball-milled to form a smooth uniform dispersion. The dispersion is then applied at a thickness of 3 mils to a 50-lb. basis weight black radiation-absorbent cellulosic paper containing approximately one quarter its weight of carbon black and about 4% of a butadiene-styrene copolymer serving as a polymeric binder. The solution is thoroughly dried with a jet of hot air. The resulting waxy

translucent durable blue coating on the black radiation-absorptive backing provides a transfer sheet.

A typewritten onion-skin paper original is placed with its reverse or unprinted side smoothly in contact with the wax-coated surface of the transfer sheet. Ultraviolet light from a BH–6 lamp held six inches away is directed for two minutes through the onion-skin original onto the wax-coated surface. The typewritten original is then replaced by a 25-lb. map overlay tracing paper receptor sheet, and the composite is subjected briefly to intense radiation in a thermographic copying machine. The two sheets are then separated. There is obtained a copy of the original consisting of blue images on the back surface of the receptor, and forming a right-reading copy as viewed through the transparent paper. Three additional high contrast copies on separate sheets of the transparent receptor paper are similarly prepared fom the same transfer sheet.

The transfer sheet prepared in accordance with this example provides copies of exceptionally clean background areas to thus increase overall copy contrast.

Other visually transparent or translucent flexible heat-resistant receptor sheets, e.g., thin paper, cellulosic films, vinyl films and the like are similarly useful.

With ethyl cellulose, polyvinyl toluene, polymethyl methacrylate or other conventional inert binder materials substituted for the polyvinyl cinnamate photosensitive material in the wax coating of the transfer sheet, under the copying procedure just described, no copy of the typewritten original results; instead, the entire surface of the wax coating transfers to the receptor.

Example 9

In the chemical type copy-sheet the photosensitive material may be present with one or another or both of the color-forming reactants to provide a heat-sensitive copy-sheet which is stabilizable by actinic irradiation.

Twenty-five parts by weight of a mixture of equal mol percent of silver behenate and behenic acid, forty-five parts of polyvinyl cinnamate as described in Example 1, two and one-half parts of 1-(2H)-phthalazinone and five hundred parts of methyl ethyl ketone are ball-milled together for 16 hours to provide a uniform fine dispersion. This dispersion is coated at a thickness of 2 mils onto 50-lb. basis weight opaque bond paper, and dried in subdued light. A 1-mil coating of a solution consisting of one part by weight ethyl cellulose, one part freshly prepared spiroindane, and ten parts methyl ethyl ketone is applied upon the first coating and the product is dried under subdued light at room temperature to provide a white heat-sensitive copy-sheet.

A graphic original typewritten on thin translucent onion-skin paper is placed smoothly in contact with the white copy-sheet prepared as just described and briefly exposed to intense radiant energy in accordance with the thermographic copying process, producing a copy of the original having blue-black letters on a white background. Two identical copies are thus prepared. The ultraviolet radiation of a BH–6 lamp held six inches away is applied for one minute to the imaged side of one of the copies. The copies are then tested for sensitivity to heat. The white background area of the ultraviolet exposed copy does not become visibly changed upon momentary contact with a metal test bar heated to 180° C. or to heat-images as conventionally developed during the thermographic copying process. However, the white background area of the unexposed copy is visibly darkened immediately upon contact with a 130° C. test bar.

Additional desensitized copies are prepared from the same thin translucent original by first exposing the white copy-sheet through the original to ultraviolet radiation of the intensity and duration previously described and then uniformly heating the selectively irradiated copy-sheet to 140° C.

A similarly useful copy-sheet is obtained by thoroughly mixing 30 parts of the silver soap dispersion with 14 parts of the spiroindane solution and coating the resultant mixture at a thickness of 3 mils onto 50-lb. basis weight opaque bond paper, and drying under subdued light at room temperature.

Analogous results are obtained by repeating this entire example with nickel stearate, stearic acid and dibenzyl dithiooxamide substituted for the silver behenate, behenic acid and spiroindane, respectively.

Example 10

This example illustrates the effectiveness of the photosensitive material in admixture with a conventional inert polymeric binder in a two-member desensitizable heat-sensitive copy-sheet product of the chemically reactive type.

Six parts by weight of a mixture of equal mol percent of silver behenate and behenic acid is dispersed in a solution of four parts of polystyrene resin in fifty parts ethyl acetate by grinding in a ball mill for 16 hours to provide a uniform and very fine dispersion. This dispersion is coated at a thickness of 2 mils onto 50-lb. basis weight opaque bond paper and dried. A coating consisting of one part polyvinyl cinnamate, one part polyvinyl toluene, and four parts methyl ethyl ketone is applied at a thickness of one mil over the first coating and dried in subdued light to complete the preparation of a white receptor or image-sheet.

A graphic original typewritten on thin translucent onionskin paper is held smoothly in contact over the coated side of the image-sheet, and a portion of the sheet is selectively irradiated for one minute through the graphic original with the ultraviolet radiation of a BH–6 lamp held 6 inches away. The remaining portion of the two-sheet combination is protected from the ultraviolet radiation with a suitable opaque shield.

A source sheet is provided by coating one-mil "Mylar" tensilized polyester film at 3 mils with a solution consisting of:

	Parts
4-methoxy-1-hydroxy naphthalene	10
Ethyl cellulose	40
Methyl ethyl ketone	350

The coating is dried in subdued light at room temperature.

The coated side of the selectively irradiated image-sheet is placed in heat-conductive contact with the coated side of the source sheet and the combination is held in contact with a metal platen heated to 140° C. A high-contrast reproduction of the typewritten original appears on the irradiated portion of the white image sheet. The non-irradiated protected portion becomes uniformly discolored with no evidence of discernible images thereon.

Image formation may alternatively be achieved by first heating a composite of source sheet and image sheet at image areas to obtain localized reaction and provide a visible copy, and then desensitizing the background areas of the image sheet by overall exposure to ultraviolet.

Example 11

In this example a photosensitive material is placed as a spacing or separating layer between layers of visibly inter-reactive chemical components in conventional inert polymeric binders in the preparation of a heat-sensitive copy-sheet which may subsequently be employed as an image transfer sheet in making further reproductions.

Ten parts by weight of a mixture of equal mol percent of silver behenate and behenic acid, one part of 1-(2H)-phthalazinone, three parts of "Parapol S–50L" styrene-isobutylene copolymer, and 86 parts of commercial grade heptane are ball-milled together for 16 hours to provide a uniform fine dispersion. This dispersion is coated at a thickness of 1 mil onto a 1-mil transparent "Mylar" tensilized polyester film backing, and dried. A coating of a 20% solution of photosensitive polyvinyl cinnamate in methyl ethyl ketone is applied at a thickness of 1.5 mils over the first coating, and dried under conditions of subdued light. A third coating is then applied at a thickness of 3 mils and consisting of a uniform mixture of 2 parts freshly prepared spiroindane, 2 parts of dithiooxamide, 4 parts of "Siloid 244" finely powdered silicon dioxide, 7.4 parts "Pliolite VT" polyvinyl toluene resin, and 86 parts of commercial grade heptane. The sheet is again dried under conditions of subdued light at room temperature to produce a heat-sensitive copy-sheet material which is desensitizable by actinic radiation.

The coated copy-sheet material is placed with its coated surface in contact with a graphic original of which a copy is desired, in this case an original typewritten on opaque paper, and the composite is subjected briefly to intense radiation rich in infra-red, applied through the sheet in accordance with thermographic front-printing procedures. A right-reading copy as viewed through the transparent backing, having infra-red-absorptive blue-black image areas on a translucent background, is obtained.

A portion of the imaged surface of the copy is next irradiated for three minutes with ultraviolet light from a BH–6 high pressure mercury arc lamp held six inches away. The remaining area is protected from the ultraviolet radiation with a suitable shield. The protected background areas remain visibly heat-sensitive when briefly subjected to a 140° C. test bar; the irradiated background areas are found to be stabilized against visible change on brief contact with a test bar heated to 155° C.

The copy thus formed has further utility in the preparation of additional reproductions on prepared receptor paper. The imaged coated surface of the sheet is placed in contact with the coated surface of a receptor sheet consisting of 50-lb. basis white opaque bond paper having a coating of the dried residue of a 1-mil layer of a ball-milled mixture of 3 parts of nickel stearate, 2 parts of "Siloid 244" silicon dioxide, 4 parts of "Lemac 1000" polyvinyl acetate resin, and 46 parts of methyl ethyl ketone. The composite is subjected to brief exposure to intense irradiation applied through the transparent film surface of the imaged copy-sheet and in accordance with the thermographic copying process, producing a further copy, in the form of black image areas against a clean white background, on the receptor sheet. In this first reproduction of the initial copy, the letter images obtained from the ultraviolet treated and the non-treated areas of the copy-sheet are of identical high quality.

Additional reproductions are made on further receptor sheets by repetition of the process described. After the first few copies, the letter images in the areas corresponding to the areas of the copy-sheet shielded from ultraviolet irradiation are found to be noticeably thickened and the background areas partially darkened, the deterioration of quality becoming increasingly apparent in further copies; whereas in the areas corresponding to the ultraviolet-treated areas of the copy-sheet, the images remain clear and sharp and the background areas remain unchanged through as many as twenty or more of such reproductions.

Many normally non-liquid polymeric organic film-forming materials which are further polymerized or cross-linked on exposure to actinic radiation have previously been described, and such polymers which are in addition normally thermoplastic, stable under prolonged storage in the absence of such radiation, non-volatile and non-decomposing under copy-sheet storage and use conditions, and preferably colorless or only slightly colored, are all found to be useful photosensitive materials in the practice of the invention. These include: soluble solid thermoplastic photocrosslinkable polycondensation products of glycols, such as decamethylene glycol, with unsaturated dicarboxylic acids such as cinnamylidenemalonic acid, crotonylidenemalonic acid, o-nitrocinnamylidene-malonic acid, naphthyl allylidenemalonic acid, and

N-methylquinolidene-2-ethylidenemalonic acid; the soluble solid thermoplastic photocrosslinkable reaction product of vinyl acetate and vinylazidophthalate with or without small proportions of vinyl alcohol residues; the soluble solid thermoplastic photocrosslinkable polymeric reaction products of acetophenone with styrene-maleic anhydride-4-(betahydroxy ethoxy)benzaldehyde or with methacrylic acid-4-(gammahydroxy propoxy)benzaldehyde intermediate products; the soluble solid thermoplastic photocrosslinkable polymeric reaction products of 4-hydroxyethoxy cinnamic acid with styrene-maleic anhydride copolymer; and the soluble solid thermoplastic photocrosslinkable polymeric reaction products of polyaminostyrene and cinnamoyl chloride.

Examples of illustrative classes and species of chemically inter-reactive image-forming materials have been provided. Many other classes of reactants suitable for heat-sensitive copy-sheet formulation have been described and are equally useful. The several components must of course be selected and applied so as to prevent or minimize pre-reaction. For example, the use of solvents or solvent systems which permit mutual solution and pre-reaction of chemical inter-reactants during coating is to be avoided. Also to be avoided are such components as tend to greatly alter or completely inhibit the desired radiation-induced polymerization or cross-linking reaction, such for example as materials having negative catalytic or inhibitor characteristics for a particular polymer or excessive amounts of opaque pigments.

Much the same considerations apply with respect to the physically convertible copy-sheets. The photosensitive material must be capable of retaining its initial physical form under normal storage and use conditions, must be susceptible of visible alteration, by appropriate modification of physical form, when briefly heated to a temperature within the range available in the thermoplastic copying process, and must be readily polymerized or cross-linked and rendered heat-resistant on exposure to actinic radiation. Where fusible components such as particulate waxes or other light-diffusing materials are to be included, it is ordinarily desirable to select particulate and polymeric materials having as nearly as possible the same refractive index and which in addition form non-crystallizing compatible blends.

Many, if not all, of the presently available photosensitive polymeric binder materials useful in the practice of the invention are highly sensitive to actinic radiation in the ultraviolet range, being somewhat less readily susceptible to visible light. The incorporation of appropriate activating dyes or the like is known to shift the sensitivity range of such materials and such modification is contemplated as coming within the ambit of the invention. Other variations and modifications will be apparent from the foregoing description.

What is claimed is as follows:

1. A heat-sensitive copy-sheet product capable of undergoing permanent visible change on momentary contact with a heated metal test bar at a conversion temperature within the approximate range of 60 to 150° C. and of being stabilized against a said change on said contact by moderate exposure to actinic radiation, said product consisting of a composite of a source sheet and a receptor sheet component in face-to-face contact, said receptor sheet component including a surface layer comprising a normally solid organic acid salt of a noble metal, said source sheet component including a surface layer comprising an organic reducing agent for the noble metal ions, and at least one of said layers including a soluble solid thermoplastic photocrosslinkable organic film-forming polymer material which undergoes an increase in softening temperature of at least about 10° C. under exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, the softening temperature being determined with the sample between cover-glasses under a weight of 5 grams and under a uniform rate of temperature increase of 1–3° C. per minute.

2. The copy-sheet product of claim 1 in which said receptor sheet component includes a surface layer comprising a normally solid organic acid salt of silver and a protective coating of the soluble solid thermoplastic photocrosslinkable organic film-forming polymer material.

3. A receptor sheet suitable for use as a component of the heat-sensitive copy-sheet product of claim 1 and comprising a thin flexible sheet backing having a surface layer comprising a normally solid organic acid salt of silver and a protective coating of the soluble solid thermoplastic photocrosslinkable organic film-forming polymer material.

4. A heat-sensitive copy-sheet consisting essentially of a strongly colored thin flexible paper backing and an optically discontinuous and non-transparent heat-transparentizable blushed coating of a soluble solid thermoplastic transparent photocrosslinkable organic film-forming polymer materials which undergoes an increase of at least about 10° C. in softening temperature on exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, the softening temperature being determined with the sample between cover glasses under a weight of 5 grams and under a uniform rate of temperature increase of 1–3° C. per minute.

5. A heat-sensitive copy-sheet consisting essentially of a transparent thin flexible backing and an optically discontinuous and non-transparent heat-transparentizable blushed coating of a soluble solid thermoplastic transparent photocrosslinkable organic film-forming polymer material which undergoes an increase of at least about 10° C. in softening temperature on exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, the softening temperature being determined with the sample between cover glasses under a weight of 5 grams and under a uniform rate of temperature increase of 1–3° C. per minute.

6. A heat-sensitive copy-sheet consisting essentially of a thin flexible paper-like backing and a visibly heat-sensitive chemically reactive coating capable on brief heating to a conversion temperature within the approximate range of 60 to 150° C. of converting to a permanently visibly distinct appearance by chemical reaction and capable of being rendered resistant to such action by moderate exposure to actinic radiation, said coating being further characterized as including a soluble solid thermoplastic photocrosslinkable organic film-forming polymeric binder material which undergoes an increase of at least about 10° C. in softening temperature on exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, the softening temperature being determined with the sample between cover glasses under a weight of 5 grams and under a uniform rate of temperature increase of 1–3° C. per minute.

7. A heat-sensitive copy-sheet consisting essentially of a thin flexible paper-like backing and a visibly heat-sensitive chemically reactive coating capable on brief heating to a conversion temperature within the approximate range of 60 to 150° C. of converting to a permanently visibly distinct appearance by chemical reaction and capable of being rendered resistant to such action by moderate exposure to actinic radiation, said coating comprising a uniform mixture of components consisting essentially of chemical co-reactants capable of undergoing visible co-reaction at said conversion temperature maintained in heat-reactive relationship by a soluble solid thermoplastic transparent photocrosslinkable organic film-forming polymeric binder material which undergoes an increase of at least about 10° C. in softening temperature on exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, the softening temperature being determined with the sample between cover glasses under a weight of 5 grams

and under a uniform rate of temperature increase of 1–3° C. per minute.

8. A heat-sensitive copy-sheet consisting essentially of a thin flexible paper-like backing and a visibly heat-sensitive chemically reactive coating capable on brief heating to a conversion temperature within the approximate range of 60 to 150° C. of converting to a permanently visibly distinct appearance by chemical reaction and capable of being rendered resistant to such action by moderate exposure to actinic radiation, said coating comprising in order a layer of a first chemical reactant material, a thin separating layer of a soluble solid thermoplastic photosensitive organic film-forming polymeric binder material which undergoes an increase in softening temperature of at least about 10° C. on exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, and a layer of a second chemical reactant material, said first and second chemical reactant materials being capable of undergoing visible co-reaction at said conversion temperature, the softening temperature of the binder material being determined with the sample between cover glasses under a weight of 5 grams and under a uniform rate of temperature increase of 1–3° C. per minute.

9. A heat-sensitive copy-sheet consisting essentially of a thin flexible paper-like backing and a visibly heat-sensitive chemically reactive coating capable on brief heating to a conversion temperature within the approximate range of 60 to 150° C. of converting to a permanently visibly distinct appearance by chemical reaction and capable of being rendered resistant to such action

by moderate exposure to actinic radiation, said coating comprising a normally solid organic acid salt of a noble metal ion, an organic reducing agent for said metal ion, and a soluble solid thermoplastic photosensitive organic film-forming polymeric binder material which undergoes an increase in softening temperature of at least about 10° C. on exposure to actinic radiation from a BH–6 high pressure mercury arc lamp at 6 inches for 2 minutes, the softening temperature being determined with the sample between cover glasses under a weight of 5 grams and under a uniform rate of temperature increase of 1–3° C. per minute.

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